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(54) Title: REWORKABLE THERMOSETTING RESIN COMPOSITIONS

(57) Abstract

This invention relates to thermosetting resin compositions useful for mounting onto a circuit board semiconductor devices, such as chip size or chip scale packages ("CSPs"), ball grid arrays ("BGAs"), and the like, each of which having a semiconductor chip, such as large scale integration ("LSI"), on a carrier substrate. The compositions of this invention are reworkable when subjected to appropriate conditions.

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REWORKABLE THERMOSETTING RESIN COMPOSITIONS

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to thermosetting resin compositions useful for mounting onto a circuit board semiconductor devices, such as chip size or chip scale packages ("CSPs"), ball grid arrays ("BGAs"), and the like, each of which having a semiconductor chip, such as large scale integration ("LSI"), on a carrier substrate. The compositions of this invention are reworkable when subjected to appropriate conditions.

Brief Description of Related Technology

In recent years, the popularity of small-sized electronic appliances, such as camera-integrated video tape recorders ("VTRs") and portable telephone sets, has made

size reduction of LSI devices desirable. As a result, CSPs and BGAs are being used to reduce the size of packages substantially to that of bare chips. Such CSPs and BGAs improve the characteristics of the electronic device while retaining many of their operating features, thus serving to protect semiconductor bare chips, such as LSIs, and facilitate testing thereof.

Ordinarily, the CSP/BGA assembly is connected to electrical conductors on a circuit board by use of a solder connection or the like. However, when the resulting CSP/BGA/circuit board structure is exposed to thermal cycling, the reliability of the solder connection between the circuit board and the CSP/BGA often becomes suspect. Recently, after a CSP/BGA assembly is mounted on a circuit board, the space between the CSP/BGA assembly and the circuit board is often now filled with a sealing resin (often referred to as underfill sealing) in order to relieve stresses caused by thermal cycling, thereby improving heat shock properties and enhancing the reliability of the structure.

However, since thermosetting resins are typically used as the underfill sealing material, in the event of a failure after the CSP/BGA assembly is mounted on the circuit board, it is very difficult to replace the CSP/BGA assembly without destroying or scrapping the structure in its entirety.

To that end, techniques for mounting a bare chip on a circuit board are accepted as substantially similar to the mounting of a CSP/BGA assembly onto a circuit board. One such technique, disclosed in Japanese Laid-Open Patent Publication No. 102343/93, involves a mounting process where a bare chip is fixed and connected to a circuit board by use of a photocurable adhesive, where, in the event of failure, this bare chip is removed therefrom. However, this technique is limited to those instances where the circuit board includes a transparent substrate (e.g., glass) which permits exposure to light from the back side, and the resulting structure exhibits poor heat shock properties.

Japanese Laid-Open Patent Publication No. 69280/94 discloses a process where a bare chip is fixed and connected to a substrate by use of a resin capable of hardening at a predetermined temperature. In the event of failure, this bare chip is removed from the substrate by softening the resin at a temperature higher than the predetermined temperature. However, no specific resin is disclosed, and there is no disclosure about treating the resin which remains on the substrate. Thus, the disclosed process is at best incomplete.

As pointed out in Japanese Laid-Open Patent Publication No. 77264/94, it is conventional to use a solvent to remove residual resin from a circuit board. However, swelling the resin with a solvent is a time consuming process and the corrosive organic acid ordinarily used as the solvent may reduce the reliability of the circuit board. Instead, that disclosure speaks to a method for removing residual resin by irradiation with electromagnetic radiation.

Japanese Laid-Open Patent Publication No. 251516/93 also discloses a mounting process using bisphenol A type epoxy resin (CV5183 or CV5183S; manufactured by Matsushita Electric Industrial Co., Ltd.). However, the removal process so disclosed does not consistently permit easy removal of the chip, the curing step is lengthy at elevated temperatures, and the process generally results in poor productivity.

Of course, mechanical methods of removing/replacing semiconductor chips from/on a substrate are known, such as by cutting the chip to be removed/replaced. See U.S. Patent No. 5,355,580 (Tsukada).

Thermoplastic underfill resins are known for use in semiconductor chip attachment. See U.S. Patent No. 5,783,867 (Belke, Jr.). However, such thermoplastic resins tend to leak under relatively modest temperature conditions. In contrast, thermosetting resins cure into a matrix which ordinarily have greater thermal stability under end use operating temperatures.

U.S. Patent Nos. 5,512,613 (Afzali-Ardakani) and 5,560,934 (Afzali-Ardakani), each refer to a reworkable thermoset composition based on a diepoxide component in which the organic linking moiety connecting the two epoxy groups of the diepoxide includes an acid cleavable acyclic acetal group. With such acid cleavable acyclic acetal groups forming the bases of the reworkable composition, a cured thermoset need only be introduced to an acidic environment in order to achieve softening and a loss of much of its adhesiveness.

U.S. Patent No. 5,872,158 (Kuczynski) refers to thermosetting compositions capable of curing upon exposure to actinic radiation, which are based on acetal diacrylates, and reaction products of which are reported to be soluble in dilute acid.

U.S. Patent No. 5,760,337 (Iyer) refers to thermally reworkable crosslinked resins to fill the gap created between a semiconductor device and a substrate to which it is attached. These resins are produced by reacting a dienophile (with a functionality greater than 1) with a 2.5-dialkyl substituted furan-containing polymer.

International Patent Publication No. PCT/US98/00858 refers to a thermosetting resin composition capable of sealing underfilling between a semiconductor device including a semiconductor chip mounted on a carrier substrate and a circuit board to which said semiconductor device is electrically connected. The composition includes about 100 parts by weight of an epoxy resin, about 3 to about 60 parts by weight of a curing agent, and about 1 to about 90 parts by weight of a plasticizer. Here, the area around the cured thermoset is to be heated at a temperature of about 190 to about 260°C for a period of time ranging from about 10 seconds to about 1 minute in order to achieve softening and a loss of much of its adhesiveness.

Notwithstanding the state of the art, it would be desirable for an underfilling sealing material to provide good productivity and thermal shock properties, while allowing the substrates with which it is to be used to be readily processed and easily separated from a semiconductor

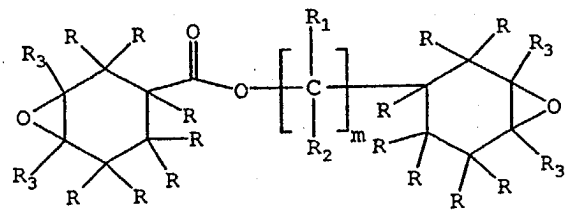
device without application of acidic media or elevated temperature conditions that may compromise the integrity of the semiconductor devices remaining on the substrate or the substrate itself.

SUMMARY OF THE INVENTION

The thermosetting resin composition, which is used as an underfill sealant between a semiconductor device and a circuit board to which the semiconductor device is electrically connected, includes broadly a curable resin component an epoxy resin component, a portion of which is an epoxy compound having at least one thermally cleavable linkage; an optional inorganic filler component; and a curing agent component including an anhydride component, a nitrogen-containing component, such as an amine compound, an amide compound, and/or an imidazole compound, and combinations thereof.

Reaction products of these compositions are capable of softening under exposure to elevated temperature conditions, such as in excess of the tempertures used to cure the composition. Such temperature exposure combined with the epoxy compound having at least one thermally cleavable linkage provides the reworkable aspect of this invention. The remaining components, discussed below, provide the physical properties and characteristics for the compositions and reaction products to render the compositions attractive for commercial use, particularly in the microelectronics industry.

The epoxy compounds with at least one thermally cleavable linkage may be chosen from those within the following formula:



I

where each R is independently selected from hydrogen, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, C_{1-4} alkoxy, halogen, cyano and nitro, and each R_3 is independently selected from hydrogen, methyl, ethyl, propyl, and isopropyl, R_1 and R_2 are each independently selected from hydrogen, methyl, ethyl, propyl, phenyl, tolyl, and benzyl, provided that both R_1 and R_2 cannot be hydrogen and m is 0 or 1. Particularly desirable epoxy compounds within formula I are given in the section entitled "Detailed Description of the Invention", which follows hereinafter.

The inventive thermosetting resin composition is useful as an underfilling sealing resin, and enables a semiconductor device, such as a CSP/BGA assembly which includes a semiconductor chip mounted on a carrier substrate, to be securely connected to a circuit board by short-time heat curing and with good productivity. Reaction products of the inventive compositions demonstrate excellent heat shock properties (or thermal cycle properties), and permit the semiconductor device to be easily removed from the circuit board by localized heating in the event of semiconductor device or connection failure. This makes it possible to reuse the circuit board (with the remaining functioning semiconductor devices still electrically attached) and thereby achieve an improvement in the yield of the production process and a reduction in production cost.

The compositions of this invention may also be used for microelectronic applications beyond sealing underfill, such as with glob top, die attachment and other applications for thermosetting compositions in which rapid cure time and an extended useful working life are desirable.

Other benefits and advantages of the present invention will become more readily apparent after a reading of the "Detailed Description" section together with the figures.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 depicts a cross-sectional view showing an example of the mounting structure in which the thermosetting resin composition of the present invention is used.

FIG. 2 depicts a flow diagram of a procedure useful to rework a cured thermosetting resin composition in accordance with the present invention, so as to remove a semiconductor device from a circuit board to which it had been attached.

DETAILED DESCRIPTION OF THE INVENTION

As noted above, the thermosetting resin compositions which are useful as underfill sealants between a semiconductor device and a circuit board to which the semiconductor device is electrically connected, includes broadly (a) an epoxy resin component, a portion of which is an epoxy compound having at least one thermally cleavable linkage; (b) an optional inorganic filler component; and (c) a curing agent component including an anhydride component, a nitrogen-containing component, such as an amine compound, an amide compound, and/or an imidazole compound, and/or combinations thereof. Reaction products of these compositions are capable of softening under exposure to elevated temperature conditions, such as in excess of the temperature chosen to cure the composition. Loss of adhesion to the substrate occurs at temperatures greater than that which was used to cure the composition. For instance, at least about 50% of adhesion to the substrate is typically lost at temperatures in excess of about 200°C.

Typically, the composition includes about 10 to about 60 weight percent of the epoxy resin component by weight of the total composition, of which about 25 to about 75 weight percent thereof is comprised of an epoxy compound having at least one thermally cleavable linkage; about 0 to about 60 weight percent of the inorganic filler component; and 0.01 to about 60 weight percent of the curing agent component, of which about 0 to about 60 weight percent thereof is comprised of an anhydride compound, 0 to about 5

weight percent thereof is comprised of an amide compound, such as a cyano-functionalized amide, like dicyandamide, and 0 to about 2 weight percent thereof is comprised of an imidazole compound.

Of course, depending on the particular set of properties desirable for a composition destined for a specific purpose these values may vary somewhat. Such variation may be achieved without undue experimentation by those persons skilled in the art, and accordingly are contemplated within the scope of the present invention.

The epoxy resin component of the present invention may include any common epoxy resin, such as a multifunctional epoxy resin. Ordinarily, the multifunctional epoxy resin should be included in an amount within the range of about 15 weight percent to about 75 weight percent of the total of the epoxy resin component. In the case of bisphenol-F-type epoxy resin, desirably the amount thereof should be in the range of from about 35 to about 65 weight percent, such as about 40 to about 50 weight percent of the total of the epoxy resin component.

Examples of the multifunctional epoxy resin include bisphenol-A-type epoxy resin, bisphenol-F-type epoxy resin (such as RE-404-S from Nippon Kayaku, Japan), phenol novolac-type epoxy resin, and cresol novolac-type epoxy from resin (such as "ARALDITE" ECN 1871 from Ciba Specialty Chemicals, Hawthorne, New York).

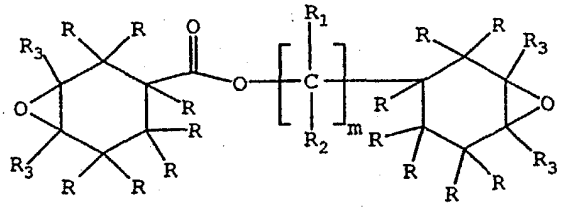
Other suitable epoxy resins include polyepoxy compounds based on aromatic amines and epichlorohydrin, such as N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenyl methane; N-diglycidyl-4-aminophenyl glycidyl ether; and N,N,N',N'-tetraglycidyl-1,3-propylene bis-4-aminobenzoate.

Among the epoxy resins suitable for use herein also include polyglycidyl derivatives of phenolic compounds, such as those available commercially under the tradename "EPON", such as "EPON" 828, "EPON" 1001, "EPON" 1009, and "EPON" 1031 from Shell Chemical Co.; "DER" 331, "DER" 332, "DER" 334, and "DER" 542 from Dow Chemical Co.; and BREN-S from Nippon Kayaku. Other suitable epoxy resins include polyepoxides prepared from polyols and the like and

polyglycidyl derivatives of phenol-formaldehyde novolacs, the latter of which are available commercially under the tradename "DEN", such as "DEN" 431, "DEN" 438, and "DEN" 439 from Dow Chemical. Cresol analogs are also available commercially under the tradename "ARALDITE", such as "ARALDITE" ECN 1235, "ARALDITE" ECN 1273, and "ARALDITE" ECN 1299 from Ciba Specialty Chemicals Corporation. SU-8 is a bisphenol-A-type epoxy novolac available from Interez, Inc. Polyglycidyl adducts of amines, aminoalcohols and polycarboxylic acids are also useful in this invention, commercially available resins of which include "GLYAMINE" 135, "GLYAMINE" 125, and "GLYAMINE" 115 from F.I.C. Corporation; "ARALDITE" MY-720, "ARALDITE" 0500, and "ARALDITE" 0510 from Ciba Specialty Chemicals and PGA-X and PGA-C from the Sherwin-Williams Co.

And of course combinations of the different epoxy resins are also desirable for use herein.

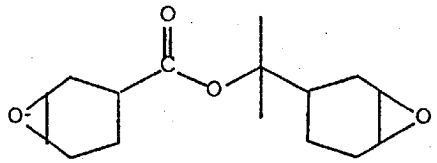
The epoxy compounds with at least one thermally cleavable linkage may be chosen from those within the following formula:



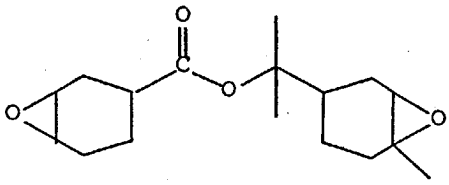
I

where each R is independently selected from hydrogen, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert butyl, C_{1-4} alkoxy, halogen, cyano and nitro, and each R_3 is independently selected from hydrogen, methyl, ethyl, propyl, and isopropyl, R_1 and R_2 are each independently selected from hydrogen, methyl, ethyl, propyl, phenyl, tolyl and benzyl, provided that both R_1 and R_2 cannot be hydrogen and m is 0 or 1.

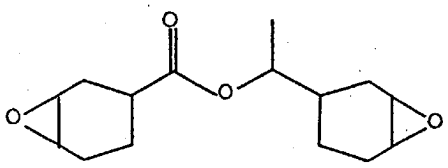
Particularly desirable epoxy compounds within formula I include:



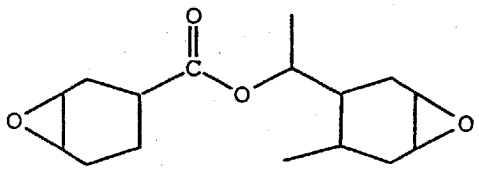
II



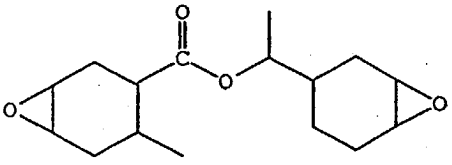
III



IV



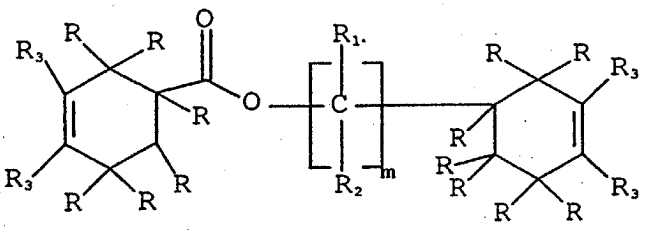
V



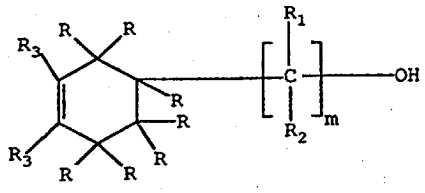
VI

The presence in the epoxy resin component of the epoxy compound(s) with at least one thermally cleavable linkage allows for repair, replacement, recovery and/or recycling of operative electronic components from assemblies that have become at least in part inoperative.

These epoxy compounds can be prepared from cycloaliphatic diene esters having the following formula

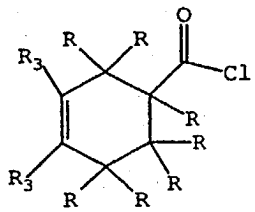


where R, R_1, R_2, R_3 and m are as given above, which themselves are the condensation product of an alcohol within formula A below:



A

where R, R_1, R_2, R_3 and m are as given above, with an acid chloride within formula B below:



B

where R and R_3 are as given above. The condensation reaction is ordinarily performed in an anhydrous polar

solvent at a temperature ranging from 0 to 20°C for a time period ranging from 6 to 18 hours.

To epoxidize the diene ester, a peracid (such as peracetic acid, perbenzoic acid, meta-chloroperbenzoic acid, and the like) may be used, with the reaction carried out until epoxidization of diene ester occurs, typically within a period of time of from 2 to 18 hours.

As an inorganic filler component, many materials are potentially useful. For instance, the inorganic filler component may often include reinforcing silicas, such as fused silicas, and may be untreated or treated so as to alter the chemical nature of their surface. Virtually any reinforcing fused silica may be used.

Particularly desirable ones have a low ion concentration and are relatively small in particle size (e.g., in the range of about 2-10 microns, such as on the order of about 2 microns), such as the silica commercially available from Admatechs, Japan under the trade designation SO-E5.

Other desirable materials for use as the inorganic filler component include those constructed of or containing aluminum oxide, silicon nitride, aluminum nitride, silica-coated aluminum nitride, boron nitride and combinations thereof.

The curing agent component should include materials capable of catalyzing the polymerization of the epoxy resin component of the inventive compositions. Desirable curing agents for use with the present invention include an anhydride component, a nitrogen-containing component, such as an amine compound, an amide compound, and an imidazole compound, and combinations thereof.

Appropriate anhydride compounds for use herein include mono- and poly-anhydrides, such as hexahydrophthalic anhydride ("HHPA") and methyl hexahydrophthalic anhydride ("MHHPA") (commercially available from Lindau Chemicals, Inc., Columbia, South Carolina, used individually or as a combination, which combination is available under the trade designation "LINDRIDE" 62C) and 5-(2,5-dioxotetrahydrol)-3-

methyl-3-cyclohexene-1,2-dicarboxylic anhydride (commercially available from ChrisKev Co., Leewood, Kansas under the trade designation B-4400).

Of course, combinations of these anhydryde compounds are also desirable for use in the compositions of the present invention.

Examples of the amine compounds include aliphatic polyamines, such as diethylenetriamine, triethylenetetramine and diethylaminopropylamine; aromatic polyamines, such as m-xylenediamine and diaminodiphenylamine; and alicyclic polyamines, such as isophoronediamine and menthenediamine.

Of course, combinations of these amine compounds are also desirable for use in the compositions of the present invention.

Examples of amide compounds include cyano-functionalized amides, such as dicyandiamide.

The imidazole compounds may be chosen from imidazole, isoimidazole, and substituted imidazoles -- such as alkyl-substituted imidazoles (e.g., 2-methyl imidazole, 2-ethyl-4-methylimidazole, 2,4-dimethylimidazole, butylimidazole, 2-heptadecenyl-4-methylimidazole, 2-methylimidazole, 2-undecenylimidazole, 1-vinyl-2-methylimidazole, 2-n-heptadecylimidazole, 2-undecylimidazole, 2-heptadecylimidazole, 2-ethyl 4-methylimidazole, 1-benzyl-2-methylimidazole, 1-propyl-2-methylimidazole, 1-cyanoethyl-2-methylimidazole, 1-cyanoethyl-2-ethyl-4-methylimidazole, 1-cyanoethyl-2-undecylimidazole, 1-cyanoethyl-2-phenylimidazole, 1-guanaminoethyl-2-methylimidazole and addition products of an imidazole and trimellitic acid, 2-n-heptadecyl-4-methylimidazole and the like, generally where each alkyl substituent contains up to about 17 carbon atoms and desirably up to about 6 carbon atoms), and aryl-substituted imidazoles [e.g., phenylimidazole, benzylimidazole, 2-methyl-4,5-diphenylimidazole, 2,3,5-triphenylimidazole, 2-styrylimidazole, 1-(dodecyl benzyl)-2-methylimidazole, 2-(2-hydroxyl-4-t-butylphenyl)-4,5-diphenylimidazole, 2-(2-methoxyphenyl)-4,5-diphenylimidazole, 2-(3-hydroxyphenyl)-4,5-diphenylimidazole, 2-(p-dimethylaminophenyl)-4,5-

diphenylimidazole, 2-(2-hydroxyphenyl)-4,5-diphenylimidazole, di(4,5-diphenyl-2-imidazole)-benzene-1,4, 2-napnthyl-4,5-diphenylimidazole, 1-benzyl-2-methylimidazole, 2-p-methoxystyrylimidazole, and the like, generally where each aryl substituent contains up to about 10 carbon atoms and desirably up to about 8 carbon atoms].

Examples of commercial imidazole compounds are available from Air Products, Allentown, Pennsylvania under the trade designation "CUREZOL" 1B2MZ and from Synthron, Inc., Morganton, North Carolina under the trade designation "ACTIRON" NXJ-60.

Of course, combinations of these imidazole compounds are also desirable for use in the compositions of the present invention.

The curing agent component may be used in an amount of from about 5 to about 40 parts by weight, per 100 parts of the epoxy resin, such as from about 5 to about 40 parts by weight, per 100 parts of the epoxy resin.

In addition, the composition may also include a flowability agent, such as a silane and/or titanate.

Appropriate silanes for use herein include octyl trimethoxy silane (commercially available from OSI Specialties Co., Danbury, Connecticut under the trade designation A-137), and methacryloxy propyl trimethoxy silane (commercially available from OSI under the trade designation A-174).

Appropriate titanates for use herein include titanium IV tetrakis [2,2-bis[(2-propenyloxy)methyl]-1-butanolato-0] [bis(ditridecylphosphito-0), dihydrogen]$_2$ (commercially available from Kenrich Petrochemical Inc., Bayonne, New Jersey under the trade designation KR-55).

When used, the flowability agent may be used in an amount of 0 to about 2 parts by weight, per 100 parts of the epoxy resin.

In addition, adhesion promoters, such as the silanes, glycidyl trimethoxysilane (commercially available from OSI under the trade designation A-187) or gamma-amino propyl triethoxysilane (commercially available from OSI under the trade designation A-1100), may be used.

Cyanate esters may also be used in the inventive compositions. The cyanate esters useful as a component in the inventive compositions may be chosen from dicyanatobenzenes, tricyanatobenzenes, dicyanatonaphthalenes, tricyanatonaphthalenes, dicyanato-biphenyl, bis(cyanatophenyl)methanes and alkyl derivatives thereof, bis(dihalocyanatophenyl)propanes, bis(cyanatophenyl)ethers, bis(cyanatophenyl)sulfides, bis(cyanatophenyl)propanes, tris(cyanatophenyl)phosphites, tris(cyanatophenyl)phosphates, bis(halocyanatophenyl)methanes, cyanated novolac, bis[cyanatophenyl(methylethylidene)]benzene, cyanated bisphenol-terminated thermoplastic oligomers, and combinations thereof.

More specifically, aryl compounds having at least one cyanate ester group on each molecule and may be generally represented by the formula $Ar(OCN)_m$, where Ar is an aromatic radical and m is an integer from 2 to 5. The aromatic radical Ar should contain at least 6 carbon atoms, and may be derived, for example, from aromatic hydrocarbons, such as benzene, biphenyl, naphthalene, anthracene, pyrene or the like. The aromatic radical Ar may also be derived from a polynuclear aromatic hydrocarbon in which at least two aromatic rings are attached to each other through a bridging group. Also included are aromatic radicals derived from novolac-type phenolic resins -- i.e., cyanate esters of these phenolic resins. The aromatic radical Ar may also contain further ring-attached, non-reactive substituents.

Examples of such cyanate esters include, for instance, 1,3-dicyanatobenzene; 1,4-dicyanatobenzene; 1,3,5-tricyanatobenzene; 1,3-, 1,4-, 1,6-, 1,8-, 2,6- or 2,7-dicyanatonaphthalene; 1,3,6-tricyanatonaphthalene; 4,4'-dicyanato-biphenyl; bis(4-cyanatophenyl)methane and 3,3',5,5'-tetramethyl bis(4-cyanatophenyl)methane; 2,2-bis(3,5-dichloro-4-cyanatophenyl)propane; 2,2-bis(3,5-dibromo-4-dicyanatophenyl)propane; bis(4-cyanatophenyl)ether; bis(4-cyanatophenyl)sulfide; 2,2-bis(4-cyanatophenyl)propane; tris(4-cyanatophenyl)-phosphite; tris(4-cyanatophenyl)phosphate; bis(3-chloro-4-

cyanatophenyl)methane; cyanated novolac; 1,3-bis[4-cyanatophenyl-1-(methylethylidene)]benzene and cyanated bisphenol-terminated polycarbonate or other thermoplastic oligomer.

Other cyanate esters include cyanates disclosed in U.S. Patent Nos. 4,477,629 and 4,528,366, the disclosure of each of which is hereby expressly incorporated herein by reference; the cyanate esters disclosed in U.K. Pat. No. 1,305,702, and the cyanate esters disclosed in International Patent Publication WO 85/02184, the disclosure of each of which is hereby expressly incorporated herein by reference. Of course, combinations of these cyanate esters within the imidazole component of the compositions of the present invention are also desirably employed herein.

A particularly desirable cyanate ester for use herein is available commercially from Ciba Specialty Chemicals, Tarrytown, New York under the tradename "AROCY" L10 [1,1-di(4-cyanatophenylethane)].

When used, the cyanate esters may be used in an amount of about 1 to about 20 weight percent based on the total amount of the epoxy resin component.

Conventional additives may also be used in the compositions of the present invention to achieve certain desired physical properties of the composition, the cured reaction product, or both.

For instance, it may be desirable in certain instances (particularly where a large volume of inorganic filler component is used) to include a reactive co-monomer component for the epoxy resin component, such as a reactive diluent.

Appropriate reactive diluents for use herein may include monofunctional or certain multifunctional epoxy resins. The reactive diluent should have a viscosity which is lower than that of the epoxy resin component. Ordinarily, the reactive diluent should have a viscosity less than about 250 cps. In the event such a monofunctional epoxy resin is included as a reactive diluent, such resin should be employed in an amount of up to about 50 parts based on the total of the epoxy resin component.

The monofunctional epoxy resin should have an epoxy group with an alkyl group of about 6 to about 28 carbon atoms, examples of which include C_{6-28} alkyl glycidyl ethers, C_{6-28} fatty acid glycidyl esters and C_{6-28} alkylphenol glycidyl ethers.

Commercially available monofunctional epoxy resin reactive diluents include those from Pacific Epoxy Polymers, Richmond, Michigan, under the trade designations PEP-6770 (glycidyl ester of neodecandoic acid), PEP-6740 (phenyl glycidyl ether) and PEP-6741 (butyl glycidyl ether).

Commercially available multifunctional epoxy resin reactive diluents include those from Pacific Epoxy Polymers, under the trade designations PEP-6752 (trimethylolpropane triglycidyl ether) and PEP-6760 (diglycidyl aniline).

The compositions of the present invention may further contain other additives, such as defoaming agents, leveling agents, dyes, and pigments. Moreover, photopolymerization initiators may also be incorporated therein, provided that such initiators do not adversely affect the properties of the composition or reaction products formed therefrom.

The thermosetting resin compositions of the present invention may be of the one-pack type, in which all the ingredients are mixed together, or of the two-pack type in which the curable component(s), is(are) included in one part and the curing agent is stored separately in a second part, and mixed together only prior to use.

During application, the thermosetting resin compositions according to the present invention penetrate and flow readily into the space between the semiconductor chip and the circuit board, or at least show a reduction in viscosity under heated or use conditions thus penetrating and flowing easily.

Generally, it is desirable to prepare thermosetting resin compositions of this invention by selecting the types and proportions of various components to reach a viscosity at a temperature of 25°C in the range of 500 to 70,000 cps, such as 800 to 3,000 cps, depending on the amount present (if any) of an inorganic filler

component, so as to improve its ability to penetrate into the space (e.g., of 10 to 200 μm) between the circuit board and the semiconductor device. At this viscosity, the gel times of the compositions will also be tailored to a specified period of time (such as 15 seconds, or 1 or 2 minutes) at a temperature of about 150°C. In such case, the inventive compositions should show no or substantially no increase of viscosity after a period of time of about six hours. With such a gel time, the compositions penetrate into the space (e.g., of 10 to 200 μm) between the circuit board and the semiconductor device relatively rapidly, and allow for a greater number of assemblies to be filled without observing a viscosity increase in the composition thereby rendering it less effective for application.

Reference to FIG. 1 shows a mounted structure (i.e., a FC package) in which a thermosetting resin composition of the present invention has been applied and cured.

The FC package 4 is formed by connecting a semiconductor chip (a bare chip) 2 to a carrier substrate 1 (e.g., a circuit board) and sealing the space therebetween suitably with a thermosetting resin composition 3.

More specifically, for example, in the assembly of FC semiconductor devices using SBB technology, the semiconductor chip 2 may be passed over a substrate bearing a conductive adhesive paste (such as a metal-filled epoxy) to form a layer thereof on the semiconductor chip 2. The layer is ordinarily formed by a printing mechanism. The conductive adhesive paste may be applied on either the carrier substrate or the semiconductor chip. One way to do this is with the stencil claimed and described in International Patent Publication No. PCT/FR95/00898. Alternatively, this connection may also be made by an anisotropically conductive adhesive. See International Patent Publication No. PCT/US97/13677.

Thereafter, the semiconductor chip 2 is positioned over the carrier substrate 1 in such a manner so that the semiconductor chip 2 is in alignment with the electrodes 5 and 6 on the carrier substrate 1, now coated with a

patterned layer of conductive adhesive paste or solder, 7 and 8. The conductive adhesive paste may be cured by a variety of ways, though ordinarily a heat cure mechanism is employed.

In order to improve reliability, the space between the semiconductor chip 2 and the carrier substrate 1 is sealed with a thermosetting resin composition 3. The cured product of the thermosetting resin composition should completely fill that space.

The semiconductor ship ordinarily may be coated with a polyimide-, benzocyclobutane- or silicone nitride-based material to passivate environmental corrosion.

Carrier substrates may be constructed from ceramic substrates of Al_2O_3, SiN_3 and mullite (Al_2O_3-SiO_2); substrates or tapes of heat-resistant resins, such as polyimides; glass-reinforced epoxy; ABS and phenolic substrates which are also used commonly as circuit boards; and the like. Any electrical connection of the semiconductor chip to the carrier substrate may be used, such as connection by a high-melting solder or electrically (or anisotropically) conductive adhesive and the like. In order to facilitate connections, particularly in SBB technology, the electrodes may be formed as wire bond bumps.

After the semiconductor chip is electrically connected to the carrier substrate, the resulting structure is ordinarily subjected to a continuity test or the like. After passing such test, the semiconductor chip may be fixed thereto with a thermosetting resin composition, as described below. In this way, in the event of a failure, the semiconductor chip may be removed before it is fixed to the carrier substrate with the thermosetting resin composition.

Using a suitable application means, such as a dispenser, a thermosetting resin composition in accordance with this invention is applied to the periphery of the electronically-connected semiconductor chip. The composition penetrates by capillary action into the space between the carrier substrate and the semiconductor chip.

The thermosetting resin composition is then thermally cured by the application of heat. During the

early stage of this heating, the thermosetting resin composition shows a significant reduction in viscosity and hence an increase in fluidity, so that it more easily penetrates into the space between the carrier substrate and the semiconductor chip. Moreover, by preheating the carrier substrate, the thermosetting resin composition is allowed to penetrate fully into the entire space between the carrier substrate and the semiconductor chip.

Thermosetting resin compositions of the present invention may ordinarily be cured by heating to a temperature in the range of about 120 to about 180°C for a period of time of about 0.5 to 30 minutes. However, generally after application of the composition, an initial cure time of about 1 minute sets up the composition, and complete cure is observed after about 5 to about 15 minutes at 165°C. Thus, the composition of the present invention can be used at relatively moderate temperatures and short-time curing conditions, and hence achieve very good productivity.

The amount of thermosetting resin composition applied should be suitably adjusted so as to fill almost completely the space between the carrier substrate and the semiconductor chip, which amount of course may vary depending on application.

Cured reaction products of the thermosetting resin compositions of the present invention demonstrate excellent adhesive force, heat resistance and electric properties, and acceptable mechanical properties, such as flex-cracking resistance, chemical resistance, moisture resistance and the like, for the applications for which they are used herein.

In the mounting process by using the thermosetting resin composition of the present invention, after the semiconductor device is mounted on the circuit board as described above, the resulting structure is tested with respect to characteristics of the semiconductor device, connection between the semiconductor device and the circuit board, other electrical characteristics, and the state of sealing. In the event a failure is found, repair can be

made in the following manner and as shown in the flow diagram depicted in FIG. 2.

The area around the semiconductor device which has failed is heated at a temperature of about 190 to about 260°C for a period of time ranging from about 10 seconds to about 1 minute. (See FIG. 2, step 1.) Desirably, the temperature should be maintained in the range of about 210 to about 220°C and the period of time should be within the 30 seconds to 1 minute range. Although no particular limitation is placed on the way in which heating occurs, localized heating is particularly desirable, such as the application of hot air to the failure site by a heating gun.

As soon as the solder is melted and the resin is softened by partial decomposition to cause a reduction in bond strength, the semiconductor device may be pulled apart and removed from the substrate, such as with tweezers or pliers.

After the semiconductor device 4 is removed, a residue of the cured reaction product of the thermosetting resin composition and a residue of the solder are left on the circuit board 5. The residue of the cured product of the thermosetting resin composition can be removed, for example, by scraping it off after the residue has been softened by heating it to a predetermined temperature.

The residue of the solder can be removed, for example, by use of a solder-absorbing braided wire. (See FIG. 2, step 2.)

Finally, a new semiconductor chip may be mounted again onto the circuit board (which has been cleaned as described above) in the manner as described above. (See FIG. 2, step 3.) Following mounting, a thermosetting resin composition in accordance with this invention may be dispensed in the area between the semiconductor device and the circuit board. (See FIG. 2, step 4.) Repair of the failure site is thus completed.

Where a failure site is found in the circuit board, the semiconductor device can be reused by removing the residue of the cured reaction product of the thermosetting resin composition and the residue of the

solder left on the bottom of the semiconductor device in the same manner as described above.

The present invention will be more readily appreciated with reference to the examples which follow.

EXAMPLES

In these examples, compositions in accordance with the present invention were prepared and evaluated for performance.

Thermosetting Resin Composition

A thermosetting resin composition in accordance with this invention was prepared by mixing together in accordance with this invention for a period of time of about 10 minutes at room temperature in an open vessel the following components in the order noted:

1. an epoxy resin component including

24.95 grams of bisphenol-F-type epoxy resin (commercially available from Nippon Kayaku under the trade designation RE-404-S), and

24.95 grams of the epoxy compound having at least one thermally cleavable linkage represented by formula III; and

2. a curing agent component including

0.2 grams of an imidazole component (commercially available from Air Products under the trade designation "CUREZOL" 1B2MZ), and

50 grams of an anhydride component comprised of 42.42 grams of a mixture in an 50:50 ratio of "HHPA" and "MHHPA" anhydrides (commercially available from Lindau under the trade designation "LINDRIDE" 62C), and 7.48 grams of a cycloaliphatic dianhydride (commercially available from ChrisKev under the trade designation B-4400).

Seven other formulations (Sample Nos. 2-8) were prepared having the following components in the amounts noted below in Table 1.

Table 1

Component		Sample No./Amount (grams)						
Type	Identity	2	3	4	5	6	7	8
Epoxy Resin	RE-404-S	19.96	11.9	13.94	26.11	26.09	7.89	14.82
	Epoxy V	29.94	17.9	20.91	39.17	39.14	11.84	22.24
Inorganic Filler Component	SO-E5 (Silica)	--	40	29.88	30	29.98	60	60
Curing Agent Component	CG-1400 (Dicyandiamide)	--	--	--	3.14	3.14	--	1.78
	1B2MZ (Imidazole)	0.2	0.12	0.14	--	--	0.08	--
	NXJ-60 (Imidazole)	--	--	--	1.4	1.4	--	0.79
	LINDRIDE 62C (Anhydride)	42.42	25.3	29.62	--	--	16.77	--
	B-4400 (Anhydride)	7.48	4.5	5.23	--	--	2.96	--
Flowability Agent	A-137 (Silane)	--	0.08	0.06	0.06	0.06	0.12	0.12
	A-187 (Silane)	--	0.08	0.06	0.06	0.06	0.12	0.12
	KR-55 (Titanate)	--	0.08	0.06	0.06	0.06	0.12	0.12
Pigment	Red Pigment	--	0.06	0.1	--	--	0.1	--
	Carbon Black	--	--	--	--	0.08	--	--

While the compositions were used upon formation (see below), they may be stored for a period of time of up to about 3 to about 6 months at a temperature of about -40°C without experiencing viscosity increase.

After formation, the composition was transferred to a 10 ml syringe made of non-reactive plastic.

Mounting Process

Using cream solder (PS10R-350A-F92C; manufactured by Harima Chemicals, Inc.), a CSP having a package of 20mm square, an electrode diameter of 0.5mm, an electrode pitch of 1.0mm, and a carrier substrate made of alumina was mounted on a 1.6mm thick glass-reinforced epoxy board having a circuit formed thereon.

Underfilling Process

The compositions of this invention may be dispensed through a 12G needle connected to the syringe into the junction between the carrier substrate and semiconductor device an assembly previously formed as above.

After such dispensing, the assembly was transferred to an oven while the temperature was maintained at about 165°C. The composition cured initially after about 1 minute, and thereafter cured completely after about 15 minutes at that temperature.

Physical Properties

The compositions have a variety of properties in both the uncured and cured state which are measurable and useful parameters for the end user in choosing a particular formulation for a desired need.

For instance, in the uncured state, the flow rate is of interest; in reaching the cured state, the adhesion and reworkability are of interest.

The flow time allows the end user to determine the rapidity with which the adhesive may be applied during a fabrication process, such as a circuit assembly operation. It may be measured by passing the composition through a 25 μm gap between glass slides aligned perpendicular to one another, using metal shims as spacers. The time required for the composition to flow between the slides is then measured at a length of about one inch, at 0.25 inch intervals. Values in seconds for the flow times of the compositions set forth above are presented as an average of three measurements below in Table 2.

The cure schedule refers to the time required for the onset of cure to occur at a certain temperatrue, in a specified period of time. This may be seen in more detail with regard to certain of the samples prepared in accordance with the present invention below in Table 2.

Table 2

Sample No.	Property				
	Flow Time (secs, .5" @100°C)	Cure Schedule (secs @165°C)	Reliability (cycles)	Adhesion (Die Pull, psi)	Tg (°C) DSC/TMA
1	9	10	900, 50% @ 1,300; L-L	1,500	139 /126
2	9	10	1,000, 50% @ 1,500; L-L	1,500	139 /117
4	16	10	900, 50% @ 1,500; A-A	1,000	/110
5	22	5	900, 50% @ 1,500; A-A	1,500	/94

In the cured state, a variety of properties are useful depending on the end use for which the composition is destined.

For instance, the adhesion provides information on the strength of the bond formed by the cured composition. The glass transition temperature ("Tg"), which is measured by differential scanning calerimetry ("DSC") or by thermal mechanical analysis ("TMA"), provides information on the hardness and strength of the cured reaction product (or, network), and its behavior with respect to changes in temperature -- that is, a higher Tg should afford a material that is better able to withstand elevated temperatures.

And of course reliability is important for the cured composition. Reliability testing is described below.

Thermal Cycling Test

Several samples (nos. 1-2 and 4-5) prepared as described above were exposed to thermal cycling tests, such as liquid-liquid thermal shock tests ("L-L") or air-air heat cycling tests ("A-A"). In the L-L tests, the samples were exposed to temperatures between -55 and 125°C, with a 5 minute dwell time at each extreme. In the A-A tests, the temperature range was the same as for the L-L test, but the dwell time was increased to 20 minutes. After a predetermined number of thermal cycles, the sample was

subjected to a continuity test to confirm the interity of the electrical connection between the CSP and the circuit board. The samples were considered to be acceptable if they passed 500 cycles L-L. Table 3 below shows collected data:

Table 3

Sample No.	L-L Test		A-A Test	
	1st Failure	50% Failure	1st Failure	50% Failure
1	900	1,300	--	--
2	1,000	1,500	--	--
4	--	--	900	1,500
5	--	--	900	1,500

As shown in Table 3, these samples are all acceptable with the type of chips tested.

Reworkability

Using a hot air generator, the area around the CSP, fixed to the circuit board with the compositions of Sample Nos. 1-2 and 4-5, should be heated by applying hot air at a temperature of about 215°C for a period of time of 1 minute. Then, the CSP may be easily removed by pulling or twisting the semiconductor chip from the circuit board using tweezers.

Thermosetting resin composition prepared without the epoxy compound having at least one thermally cleavable linkage represented by formula III, with the balance of the epoxy resin component coming from the RS-404-S epoxy resin, which was dispensed and cured as above, does not allow for removal in the manner so described.

Reliability of Replaced Chip

The cured composition left on the curcuit board after the so-described process can be removed by using physical scrapping procedures, such as using a dremel with a rotating bristle at about 30,000 rpm.

The site of the failed semiconductor chip should then be fluxed and a new semiconductor chip may be attached using conventional flip chip technology. Then, the

thermosetting resin composition of this invention may be applied around the periphary of the newly-replaced semi-conductor chip and cured by heating to a temperature of about 165°C for a period of 7 minutes.

Electrical connections were securely established on the so-repaired CSP-mounted circuit board. This new board assembly was again submitted to L-L and A-A thermal cycling tests. Observed results for Sample No. 5 are given below in Table 4.

Table 4

Sample No.	L-L Test		A-A Test	
	1st Failure	50% Failure	1st Failure	50% Failure
5	800	1,300	100	>600

The samples described above are presented as illustrative, rather than limiting, examples of the inventive compositions. Many additional embodiments thereof are included in the spirit and scope of the invention.

What Is Claimed Is:

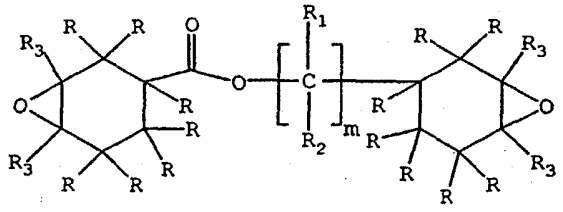
1. A thermosetting resin composition capable of sealing underfilling between a semiconductor device including a semiconductor chip mounted on a carrier substrate and a circuit board to which said semiconductor device is electrically connected, reaction products of which are capable of softening and losing their adhesiveness under exposure to temperature conditions in excess of those used to cure the composition, said composition comprising:

(a) an epoxy resin component, a portion of which comprises an epoxy compound having at least one thermally cleavable linkage;

(b) optionally, an inorganic filler component; and

(c) a curing agent component comprising a member selected from the group consisting of anhydride compounds, amine compounds, amide compounds, imidazole compounds, and combinations thereof.

2. The composition according to Claim 1, wherein the epoxy compound having at least one thermally cleavable linkage may be chosen from those within the following formula:

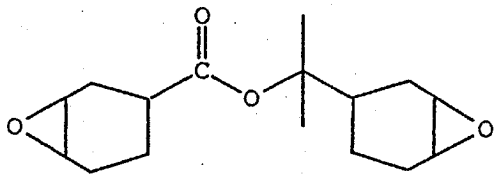


I

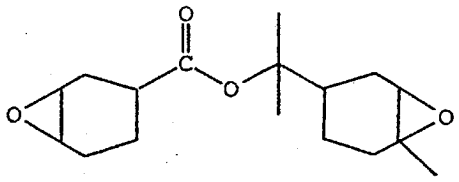
where each R is independently selected from hydrogen, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert butyl, C_{1-4} alkoxy, halogen, cyano and nitro, and each R_3 is independently selected from hydrogen, methyl, ethyl, propyl, and isopropyl, R_1 and R_2 are each independently selected

from hydrogen, methyl, ethyl and propyl, provided that both R_1 and R_2 cannot be hydrogen and m is 0 or 1.

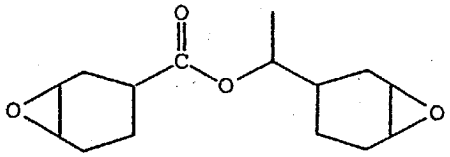
3. The composition according to Claim 2, wherein the epoxy compound having at least one thermally cleavable linkage is a member selected from the group consisting of



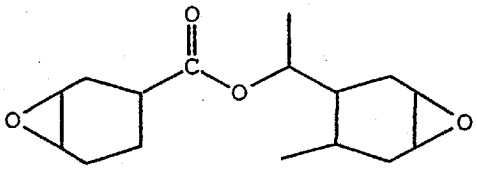
II



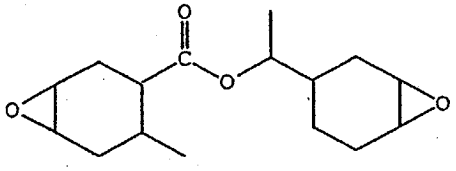
III



IV

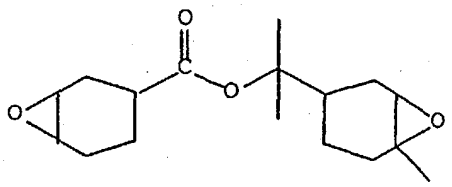


V



VI

4. The composition according to Claim 2, wherein the epoxy compound having at least on thermally cleavable linkage is:



III

5. The composition according to Claim 1, further comprising a flowability agent.

6. The composition according to Claim 5, wherein the flowability agent is a member selected from the group consisting of silanes, titanates and combinations thereof.

7. The composition according to Claim 1, further comprising an adhesion promtor.

8. The composition according to Claim 7, wherein the adhesion promoter is a member selected from the group consisting of glycidyl trimethoxysilane, gamma-amino propyl triethoxysilane, and combinations thereof.

9. The composition according to Claim 1, further comprising a cyanate ester.

10. The composition according to Claim 9, wherein the cyanate ester is a member selected from the group consisting of dicyanatobenzenes, tricyanatobenzenes, dicyanatonaphthalenes, tricyanatonaphthalenes, dicyanato-biphenyl, bis(cyanatophenyl)methanes and alkyl derivatives thereof, bis(dihalocyanatophenyl)propanes, bis(cyanatophenyl)ethers, bis(cyanatophenyl)sulfides, bis(cyanatophenyl)propanes, tris(cyanatophenyl)phosphites, tris(cyanatophenyl)phosphates, bis(halocyanatophenyl)methanes, cyanated novolac,

bis[cyanatophenyl(methylethylidene)]benzene, cyanated bisphenol-terminated thermoplastic oligomers, and combinations thereof.

11. The composition according to Claim 1, wherein the inorganic filler component may be selected from the group consisting of materials constructed of or containing reinforcing silicas, aluminum oxide, silicon nitride, aluminum nitride, silica-coated aluminum nitride, boron nitride, and combinations thereof.

12. The composition according to Claim 1, wherein the inorganic filler component has a low ion concentration and a particle size in the range of about 2-10 microns.

13. The composition according to Claim 1, wherein the anhydride compounds of the curing agent component may be selected from the group consisting of hexahydrophthalic anhydride, methyl hexahydrophthalic anhydride, 5-(2,5-dioxotetrahydrol)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride, and combinations thereof.

14. The composition according to Claim 1, wherein the amine compounds of the curing agent component may be selected from the group consisting of dicyandiamide, diethylenetriamine, triethylenetetramine, diethylaminopropylamine, m-xylenediamine, diaminodiphenylamine, isophoronediamine, menthenediamine, polyamides, and combinations thereof.

15. The composition according to Claim 1, wherein the amide compounds of the curing agent component may be selected from the group consisting of dicyandiamide and combinations thereof.

16. The composition according to Claim 1, wherein the imidazole compounds of the curing agent component may be selected from the group consisting of imidazole,

isoimidazole, 2-methyl imidazole, 2-ethyl-4-methylimidazole, 2,4-dimethylimidazole, butylimidazole, 2-heptadecenyl-4-methylimidazole, 2-methylimidazole, 2-undecenylimidazole, 1-vinyl-2-methylimidazole, 2-n-heptadecylimidazole, 2-undecylimidazole, 2-heptadecylimidazole, 2-ethyl 4-methylimidazole, 1-benzyl-2-methylimidazole, 1-propyl-2-methylimidazole, 1-cyanoethyl-2-methylimidazole, 1-cyanoethyl-2-ethyl-4-methylimidazole, 1-cyanoethyl-2-undecylimidazole, 1-cyanoethyl-2-phenylimidazole, 1-guanaminoethyl-2-methylimidazole, addition products of an imidazole and trimellitic acid, addition products of an imidazole and 2-n-heptadecyl-4-methylimidazole, phenylimidazole, benzylimidazole, 2-methyl-4,5-diphenylimidazole, 2,3,5-triphenylimidazole, 2-styrylimidazole, 1-(dodecyl benzyl)-2-methylimidazole, 2-(2-hydroxyl-4-t-butylphenyl)-4,5-diphenylimidazole, 2-(2-methoxyphenyl)-4,5-diphenylimidazole, 2-(3-hydroxyphenyl)-4-,5-diphenylimidazole, 2-(p-dimethylaminophenyl)-4,5-diphenylimidazole, 2-(2-hydroxyphenyl)-4,5-diphenylimidazole, di(4,5-diphenyl-2-imidazole)-benzene-1,4, 2-napnthyl-4,5-diphenylimidazole, 1-benzyl-2-methylimidazole, 2-p-methoxystyrylimidazole, and combinations thereof.

17. The composition according to Claim 1, wherein the curing agent component is used in an amount of from about 3 to about 60 parts by weight, per 100 parts by weight of the epoxy resin.

18. The composition according to Claim 1, wherein the curing agent component is used in an amount of from about 5 to about 40 parts by weight, per 100 parts of the epoxy resin.

19. The composition according to Claim 5, wherein the flowability agent is selected from octyl trimethoxy silane, methacryloxy propyl trimethoxy silane, titanium IV tetrakis [2,2-bis[(2-propenyloxy)methyl]-1-butanolato-0]

[bis(ditridecylphosphito-O), dihydrogen]$_2$, and combinations thereof.

20. The composition according to Claim 5, wherein the flowability agent is used in an amount up to about 2 parts by weight, per 100 parts of the epoxy resin.

21. The composition according to Claim 1, having a viscosity in the range of about 500-70,000 cps.

22. A thermosetting resin composition capable of sealing underfilling between a semiconductor device including a semiconductor chip mounted on a carrier substrate and a circuit board to which said semiconductor device is electrically connected, reaction products of which are capable of softening and losing their adhesiveness under exposure to temperature conditions in excess of those used to cure the composition, said composition comprising:

(a) an epoxy resin component, a portion of which comprises an epoxy compound having at least one thermally cleavable linkage, in an amount within the range of about 20 to 65 weight percent, based on the total weight of the composition;

(b) an inorganic filler component in an amount up to about 60 weight percent, based on the total weight of the composition;

(c) a curing agent component in an amount within the range of 2 to about 50 weight percent, based on the total weight of the composition; and

(d) a flowability agent in an amount up to about 0.5 weight percent, based on the total weight of the composition.

23. Reaction products formed from the compositions according to any one of Claims 1-22.

24. An electronic device comprising a semiconductor device and a circuit board to which said semiconductor device is electrically connected assembled using a thermosetting resin composition according to any one of Claims 1-21 as an underfill sealant between the semiconductor device and the circuit board, wherein reaction products of the composition are capable of softening and losing their adhesiveness under exposure to temperature conditions in excess of those used to cure the composition.

FIG. 1

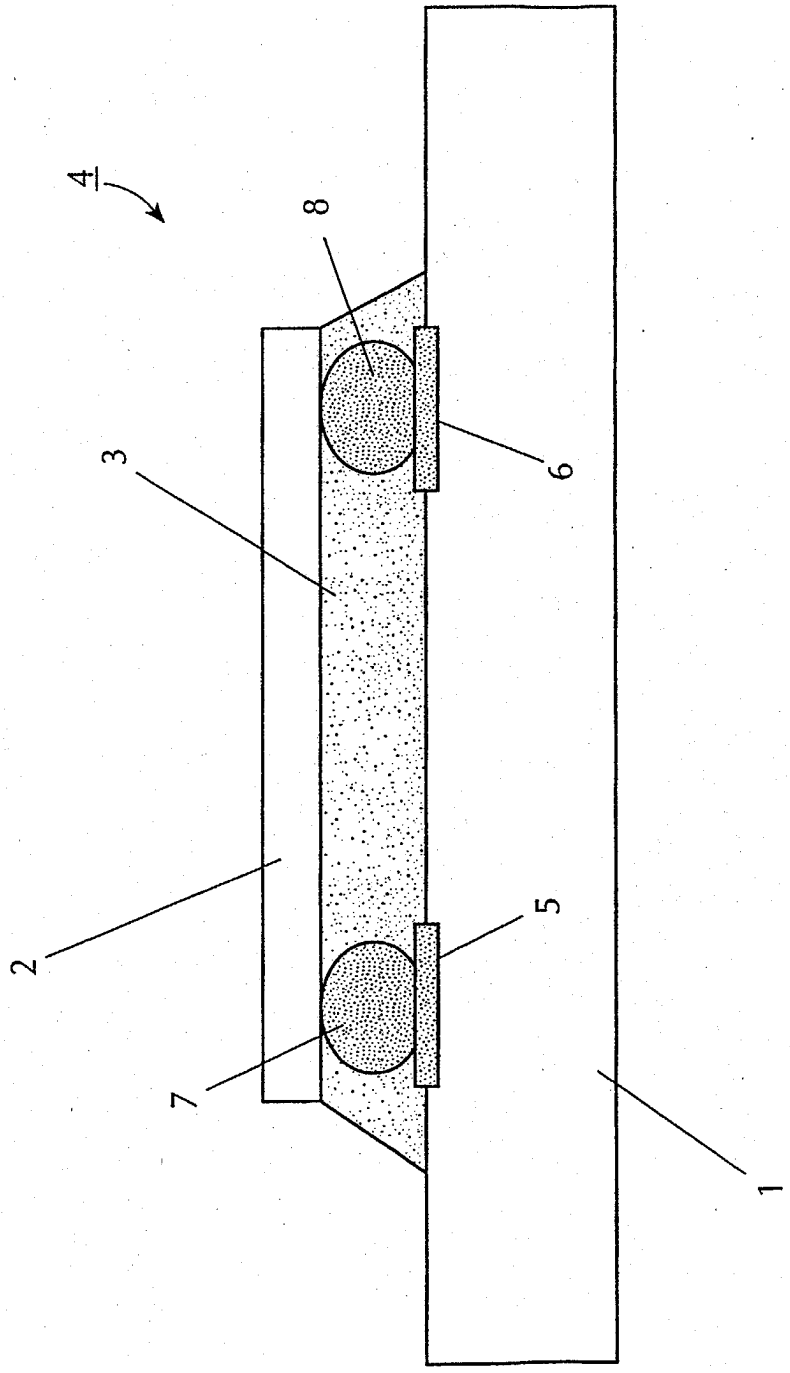
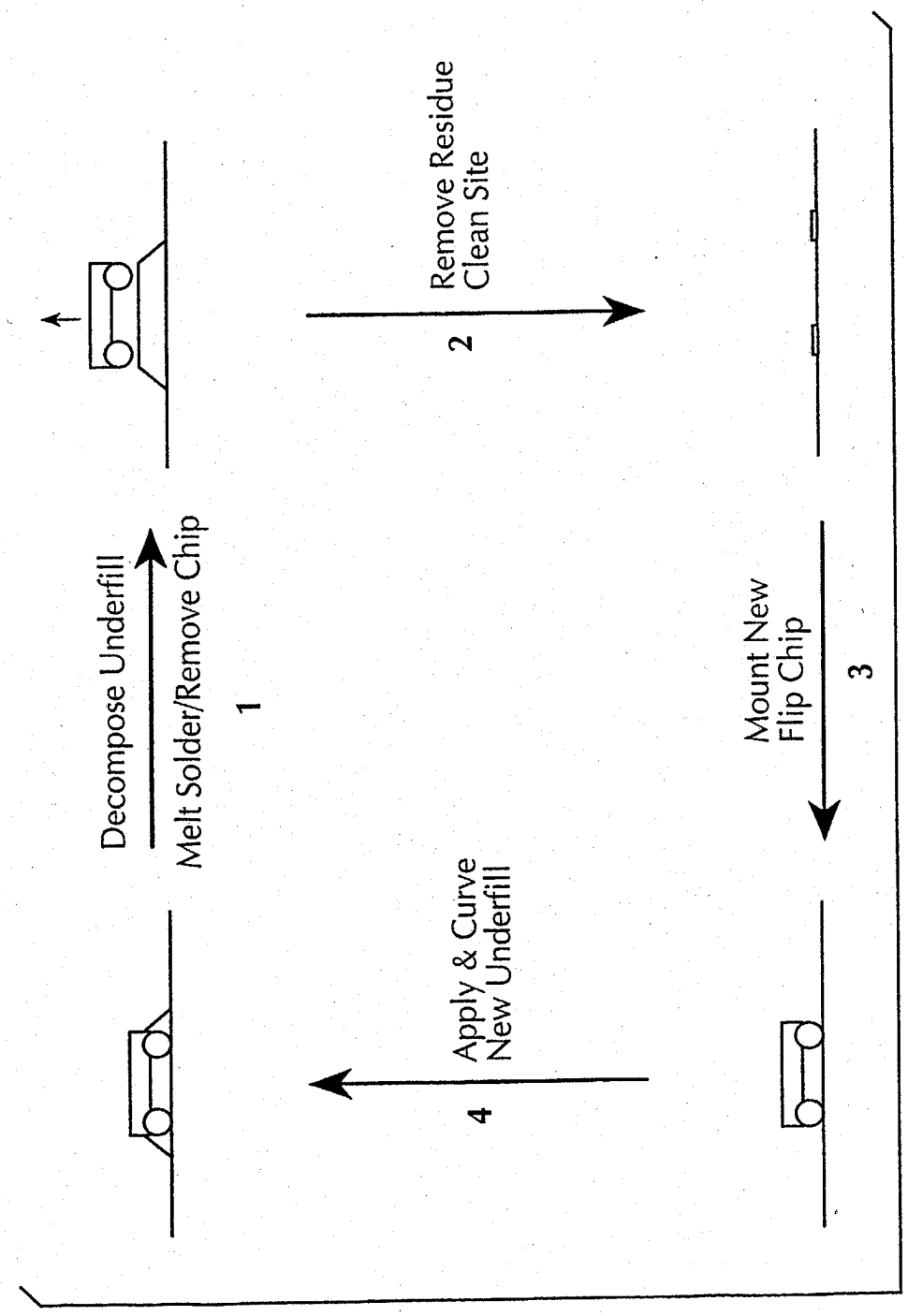


FIG. 2


Decompose Underfill
Melt Solder/Remove Chip
1
Remove Residue
Clean Site
2
Mount New
Flip Chip
3
Apply & Curve
New Underfill
4

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/US 00/07452

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G59/24 H01L21/56

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 394 192 A (CIBA-GEIGY) 24 October 1990 (1990-10-24) page 3, line 28 -page 5, line 35; claims 1,3-10	1-3
X	EP 0 105 488 A (UNION CARBIDE CORPORATION) 18 April 1984 (1984-04-18) page 1, line 26 -page 12, line 34	1-3
X	WANG &WONG: "Novel Thermally REworkable Underfill Encapsulants for Flip-Chip Applications" ELECTRONIC COMPONENTS AND TECHNOLOGY CONFERENCE, 1998, pages 92-100, XP000803604 the whole document	1

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 July 2000	04/08/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Bourgonje, A

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte onal Application No
PCT/US 00/07452

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 394192 A	24-10-1990	AT 138670 T	15-06-1996
		DE 59010345 D	04-07-1996
		ES 2087900 T	01-08-1996
		FI 96694 B	30-04-1996
		JP 2296820 A	07-12-1990
		US 5106947 A	21-04-1992
EP 105488 A	18-04-1984	AU 566647 B	29-10-1987
		AU 1974183 A	05-04-1984
		JP 1445497 C	30-06-1988
		JP 59081329 A	11-05-1984
		JP 62054338 B	14-11-1987
		MX 168518 B	27-05-1993
		NO 833537 A,B,	02-04-1984
		US 4532274 A	30-07-1985
US 5948922 A	07-09-1999	US 5973033 A	26-10-1999
EP 829502 A	18-03-1998	US 6008266 A	28-12-1999
		JP 10095833 A	14-04-1998
US 5821456 A	13-10-1998	US 5930598 A	27-07-1999

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

To:
LOCTITE CORPORATION
Attn. BAUMAN, Steven C.
1001 TROUT BROOK CROSSING
ROCKY HILL, CT 06067
UNITED STATES OF AMERICA

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL SEARCH REPORT OR THE DECLARATION

(PCT Rule 44.1)

	Date of mailing *(day/month/year)* 04/08/2000
Applicant's or agent's file reference LC-362 PCT	**FOR FURTHER ACTION** See paragraphs 1 and 4 below
International application No. PCT/US 00/ 07452	International filing date *(day/month/year)* 22/03/2000
Applicant LOCTITE CORPORATION	

1. [X] The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19:
The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Fascimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. [ ] The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. [ ] **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

[ ] the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

[ ] no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

Shortly after **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90*bis*.1 and 90*bis*.3, respectively, before the completion of the technical preparations for international publication.

Within **19 months** from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within **20 months** from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Alfredo Prein

NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international pbulication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

NOTES TO FORM PCT/ISA/220 (contin[redacted])

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped),whether

(i) the claim is unchanged;

(ii) the claim is cancelled;

(iii) the claim is new;

(iv) the claim replaces one or more claims as filed;

(v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."

2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."

3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."

4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international appplication is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	FOR FURTHER ACTION	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
LC-362 PCT		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/US 00/ 07452	22/03/2000	23/03/1999
Applicant		
LOCTITE CORPORATION		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 03 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readble form.

   [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. ___

   [ ] as suggested by the applicant.

   [ ] because the applicant failed to suggest a figure.

   [ ] because this figure better characterizes the invention.

   [ ] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/07452

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G59/24 H01L21/56

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
WPI Data, EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 394 192 A (CIBA-GEIGY) 24 October 1990 (1990-10-24) page 3, line 28 -page 5, line 35; claims 1,3-10	1-3
X	EP 0 105 488 A (UNION CARBIDE CORPORATION) 18 April 1984 (1984-04-18) page 1, line 26 -page 12, line 34	1-3
X	WANG &WONG: "Novel Thermally REworkable Underfill Encapsulants for Flip-Chip Applications" ELECTRONIC COMPONENTS AND TECHNOLOGY CONFERENCE, 1998, pages 92-100, XP000803604 the whole document	1

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 July 2000	04/08/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Bourgonje, A

1

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
P,X	US 5 948 922 A (OBER ET AL) 12 March 1996 (1996-03-12) the whole document	1-24
A	EP 0 829 502 A (INTERNATIONAL BUSINESS MACHINES CORPORATION) 18 March 1998 (1998-03-18) page 3, line 40 -page 9, line 14	1
A	US 5 821 456 A (WILLE ET AL) 13 October 1998 (1998-10-13) column 2, line 54 -column 5, line 36	1

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 394192 A	24-10-1990	AT 138670 T	15-06-1996
		DE 59010345 D	04-07-1996
		ES 2087900 T	01-08-1996
		FI 96694 B	30-04-1996
		JP 2296820 A	07-12-1990
		US 5106947 A	21-04-1992
EP 105488 A	18-04-1984	AU 566647 B	29-10-1987
		AU 1974183 A	05-04-1984
		JP 1445497 C	30-06-1988
		JP 59081329 A	11-05-1984
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		NO 833537 A,B,	02-04-1984
		US 4532274 A	30-07-1985
US 5948922 A	07-09-1999	US 5973033 A	26-10-1999
EP 829502 A	18-03-1998	US 6008266 A	28-12-1999
		JP 10095833 A	14-04-1998
US 5821456 A	13-10-1998	US 5930598 A	27-07-1999